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## (54) Coating compositions

(57) A liquid coating composition comprises water and containing reactive/curable organic resinous components, which comprises a reactive/curable organic resinous material which has also been reacted with the lipophilic portion of a surface active agent. The composition may be in the form of an emulsion of an organic liquid in water, or in the form of a dispersion of solid resinous material in water. The resin may be thermally curable or photosensitive. The composition can be used in making a patterned resist upon a substrate in the manufacture of a printed circuit board. The resins exemplified are epoxy resins and the surfactant is preferably a polyethoxylated/polypropoxylated sorbitan ester. The partially reacted epoxy resin may be thermally cured using curing agents, such as polyamines and dicyandiamide, or it may be further reacted with an ethylenically unsaturated acid, e.g. (meth) acrylic acid or maleic anhydride, to produce a UV radiation sensitive material.

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### COATING COMPOSITIONS

This invention is concerned with improvements in and relating to coating compositions. More particularly, the invention is concerned with coating compositions for application to substrates and subsequent curing thereon, in which the principal liquid carrier is water.

Broadly, the present invention provides liquid coating compositions for application to substrates and subsequent curing thereon, the compositions comprising water as principal liquid carrier and containing reactive/curable organic resinous components in which the reactive/curable organic resinous component comprises a reactive/curable organic resinous material which has also been reacted with the lipophilic (hydrophobic) portion of a surface active agent.

Coating compositions in accordance with the invention will generally be based on reactive/curable organic resinous materials which are, themselves, insoluble in water and two general classes of such compositions are contemplated, namely (i) aqueous emulsions of organic liquids (comprising the organic resinous material itself

or a solution thereof in an organic solvent), and (ii) dispersions of solid resinous material, in particulate form.

In either case, the surfactant molecules, incorporated in the resinous material, serve to aid emulsification or dispersion. As noted above, compositions in accordance with the invention comprise water as principal carrier, that is the water forms at least 60% by weight of any carrier liquid and preferably forms at least 80%, more preferably 90% by weight thereof.

Compositions in accordance with the invention are particularly useful as so-called "UV resist" compositions, particularly solder resist compositions, for use in the manufacture of printed circuit boards.

Resist compositions are used in the manufacture of printed circuit boards to form patterned layers on the surfaces of certain substrates (eg. copper - clad phenolic laminate boards) so that some areas are protected and others not protected against subsequent treatment of some sort, such as, for example, etching, plating or contact with molten solder. Resists intended for protection of parts of a substrate against solder are commonly termed solder resists.

A patterned layer of a resist may be applied to a substrate by applying a liquid in patterned form (commonly through an appropriately patterned or masked screen) and then curing the applied layer to form the final resist, for example, by exposure to radiation in the case of radiation - sensitive compositions or by thermal curing in the case of thermally curable compositions. Alternatively, using a photo-imaging technique, a layer of radiation sensitive (generally U-V sensitive) liquid coating is applied over the surface of the substrate and then, commonly after drying to form a tack-free film, image-wise exposed to appropriate radiation through an appropriately patterned mask. Depending on the nature of the photosensitive material and the resist composition, the effect of radiation may be to render it more soluble ("positive-working" resist) or less soluble (a "negative-working" resist). In general, solder resists are commonly based on negative-working photosensitive materials. In either case, after exposure to radiation, the irradiated coating is "developed" by dissolving away the more soluble portions of the coating with an appropriate solvent. Compositions in accordance with the invention, for use as resist materials, may comprise as the reactive/curable resinous material a thermally curable material and/or a radiation sensitive material. Since thermally curable compositions generally comprise a

thermally reactive organic component, together with a catalyst, curing agent or cross-linking agent potentially reactive with the thermally reactive material, it is often convenient to put such compositions up as two-part-packs, wherein the potentially reactive components of the composition are separated in different packs. In such a case, one or other of the packs may contain a radiation-sensitive component, whereby the composition may be both radiation-sensitive and thermally curable.

Alternatively, compositions in accordance with the invention may be put as one part systems.

A particularly useful class of thermally curable materials, or materials from which radiation-sensitive materials may be derived, are the so-called "epoxy resins" or epoxy compounds. Such compounds further contain reactive groups (epoxy groups) which may be used to react with complementary reactive groups, such as carboxylic acid groups, in the lipophilic portions of surfactants. Thus, in accordance with a preferred embodiment of the invention, the organic resinous materials present in the compositions of the invention comprise the partial reaction products of epoxy resins and surfactants, particularly polyethoxylated and/or polypropoxylated surfactants, containing, in their

lipophilic moiety, a carboxylic acid group. A particularly preferred class of such surfactants comprises the polyethoxylated/polypropoxylated sorbitan esters, such as those sold under the trade name Atlas G1350.

By the term "partially reacted", we mean that not all of the epoxy groups of the polyepoxy compound are reacted with the surfactant but sufficient remain, in the case of thermally curable materials, for effective subsequent thermal cure. In the case of radiation-sensitive materials derived from the polyepoxy compounds, there should, of course be sufficient free epoxy groups remaining, after reaction with the surfactant, to afford, by reaction with radiation-sensitive group-containing compounds, a material having a sufficient proportion of radiation sensitive groups to give a useful level of cure (cross-linking).

A wide variety of epoxy resins are known and these are described, for example, in "The Chemistry Of Organic Film Forms", D.H. Solomon, Robert E Krieger publishing company 1982, pages 187 - 210. Typical epoxy resins are those derived from the reaction of Bisphenol or like dihydric phenols with epichlorydrin, or the so-called Novolak epoxy resins derived from the reaction of phenol or cresol novolaks with epichlorydrin. These latter are

particularly useful in the formulation of solder resist compositions. In a thermally curable system, there must, also, be present a curing agent and suitable curing agents for use in combination with epoxy resins include polyamines, polyamino resins, dicyandiamide etc. Further, a catalyst may be employed to accelerate reaction between the epoxy resin and the curing agent, for example an imidazole or blocked imidazole compound.

Where the reactive/curable resinous material is to be radiation-sensitive this is typically an ethylenically saturated material particularly one derived from the reaction of an ethylenically unsaturated carboxylic acid, such as acrylic acid or methacrylic acid, with an epoxy resin (especially a novolak epoxy resin which has previously been partially reacted with surfactants. Preferably, the reaction product is further modified (as described in EP/A/04086229) by reaction with a dicarboxylic acid or anhydride thereof to produce a product soluble in (be developed by) aqueous alkaline solutions since this form of development is most preferred for environmental reasons.

Other ethylenically unsaturated materials may be present in radiation-sensitive compositions such as (meth) acrylic acid esters of styrene-maleic anhydride copolymers and multifunctional (meth) acrylate esters

such as tris-(2-hydroxy ethyl) isocyanurate triacylate, di-trimethylol propane, triacylate and pentaerythritol tetra-acrylate.

In order to render such ethylenically unsaturated materials sensitive to ultra-violet light, the composition will also suitably contain a photoinitiator or UV sensitiser, eg. an organic ketone such as anthraquinone, or the commercially available compound sold under the trade names Irgacure 651 or Irgacure 907 (c). In addition to the reactive/curable resinous material, compositions in accordance with the invention, may, and most commonly will, contain other components, such as inert particulate fillers, colouring agents, flow aids and defoamers. The fillers, which are generally in organic fillers are particularly useful components and examples thereof include silica, talc, alumina, calcium carbonate and barium sulphate. Compositions in accordance with the invention suitably contain from 40 to 70% by weight, preferably 55 to 60% by weight, of reactive/curable resin; from 30 to 60% by weight, preferably 50 to 60% by weight, of liquid carrier (water together with organic solvent if any); and from 2 to 8, preferably 4 to 6% by weight of minor components such as flow aids, colouring agents, etc.

As noted above, the liquid compositions of the invention take the form of emulsions or dispersions. In the case of an emulsion, the material to be emulsified is, commonly after having firstly being dissolved in an appropriate organic solvent, emulsified with the appropriate amount of water, typically using typically suitable apparatus such as a Silverson Stirrer. Thus, the material to be emulsified, is dissolved to give a relatively concentrated solution (eg. containing 50 - 80% by weight of solids) in a solvent such a glycol ether ester (eg. isopropyl cellosolve acetate). In the case of solid materials a dispersion system is employed and, in this case, the solid components are finally divided (ground) to a suitable particle size (e.g. 0.5 to 5  $\mu\text{m}$ ) and then dispersed, using suitable apparatus, in water.

In use, a composition in accordance with the invention (which may be prepared from a two-part pack system in the case of a thermally curable system) is applied to the desired substrate, generally in patterned form (through a patterned screen) for the simple thermally curable compositions, or as an overall layer for photoimageable (and optionally thermally curable) systems. In this latter case, any suitable coating system may be used, such as curtain coating, roller coating, dip coating or the like. The thickness of the

coating will, of course, depend upon the intended end use and nature of the resist; thicknesses of 20 to 80  $\mu\text{m}$  (measured as dry film thicknesses) generally proving suitable.

After application of the liquid coating composition to the substrate it is, in the case of the thermally curable systems simply cured by heating, eg at a temperature of 120 to 140°C for a period of 60 to 120 minutes. In the case of the photoimageable (optionally thermally curable) systems, the applied liquid is generally first dried to give a substantially tack-free film, image wise exposed to radiation, developed and then, optionally, finally thermally cured, for example under the conditions noted above.

In order that the invention may be well understood, the following examples are given by way of illustration only.

#### Example I

An equivalent of an epoxy novolak resin (Quatrex A410, Dow Chemicals) was dissolved in ethyl 3 - ethoxy propionate. Polyethoxylated polypropoxylated sorbitan ester surfactant (Atlas G1350, ICI) was then added in sufficient mass to give final levels of 10% total formulation weight in the finished resist. The mixture

was then heated to 110°C for 2 hours or until there was no measurable acid value remaining. The remaining, unadducted epoxy groups were quantitatively assayed by titration and an equivalent amount of acrylic acid charged in order to fully acrylate the resin. This acrylated resin was then adducted with tetrahydrophthalic anhydride to yield a resin with an acid value of 70mg KOH/g.

This resin was then used to produce a resist ink formulation by three roll milling in the following formulation:

Surfactant adducted resin (as above)	85.17 parts
Photoinitiator (Irgacure 651 Ciba Geigy)	2.30 parts
Photoinitiator (Irgacure 907 Ciba Geigy)	1.30 parts
Photoinitiator (Quantacure ITX Ward Blenkinsop)	0.90 parts
Flow Aid (Modaflow, Monsanto Inc.)	1.50 parts
Talc	6.00 parts
Silica	1.00 parts
Degassing Aid (Fluorad, Fluorochem)	0.33 parts
Pigment Dispersion (Phthalocyanin Green)	1.50 parts

This resist formulation was then warmed and dispersed by high speed stirring (Silverson high speed stirrer) into a smooth light green emulsion using the following formulation.

Resist Formulation (as above)	55 parts
Distilled Water	45 parts

The emulsified resist was then printed onto a pre-cleaned IPC solder mask test panel through a silk screen, dried at 100°C for half an hour in a ventilated, convection oven and photoimaged through suitable art work. The imaged film developed cleanly in 0.6% w/w sodium carbonate solution at 38°C. The developed film was then post dried at 150°C for 1 hour and given a final UV cure of 2000m Joules. The end product of this process was a solder resist film which showed good resolution of the artwork and resistance to the soldering process, physical hardness and solvent resistance tests generally applied to solder resists.

#### Example II

An equivalent of an epoxy cresol novolak resin (Quatrex 3710, Dow Chemicals) was dissolved in toluene. Polyethoxylated polypropoxylated sorbitan ester surfactant (Atlas G1350 ICI) was then charged to the reaction vessel in sufficient mass to give final levels of 10% total formulation weight in the finished resist. The mixture was then heated to 100°C for 2 hours when there was no measurable acid value remaining. The remaining epoxy groups were then adducted with acrylic acid. The acrylated resin was then adducted with maleic anhydride to yield a resin with an acid value of 70mg KOH/g. This resin was then vacuum stripped to yield a

solid material with a melting point of between 95°C - 99°C.

The solid resin was mixed with the formulation given below in a heated dual screen extruder to produce a green brittle product which was ground in an air mill to give particles of average size 25 µm. At the same time a solid bis-phenol A based epoxy resin was also milled down to similar particle size.

Surfactant adducted resin	82.70 parts
Photoinitiator (Irgacure 907 Ciba Geigy)	7.50
Photoinitiator (Quantacure ITX Ward Blenkinsop)	1.70
Pigment (Phthalocyanin Green)	1.00
Dichandiamide	0.10
2-Ethyl-4-Methyl Imidazole	0.50
Silica	6.50

The powdered resist formulation and powdered epoxy resin were then added to a solution of a polymeric thickener in distilled water to the following formulation:-

Powdered Resist (as above)	40.00 parts
Powdered Epoxy Resin	12.00
(Epikote 1001, Shell Chemicals)	
Polymeric Thickening Agent	
(RM8, Rohm & Haas)	8.00
Distilled Water	40.00

The mixture was then passed through a colloid mill to yield a creamy green suspension of solid particles (substantially of  $5\mu\text{m}$  or less in size).

The powder aqueous dispersion resist thus formed was screen printed onto an IPC solder resist test panel, dried and photoimaged through the relevant art work. The pattern developed quickly and cleanly in 0.6% w/w aqueous sodium carbonate solution, the developed film was then given a final thermal cure for 1.5 hours at  $150^\circ\text{C}$  to yield a solder resist film which was resistant to soldering and physical and chemical tests.

CLAIMS

1. A liquid coating composition comprising water as principal water carrier and containing reactive/curable organic resinous components, in which the reactive/curable organic resinous component comprises a reactive/curable organic resinous material which has also been reacted with the lipophilic portion of a surface active agent.
2. A composition as claimed in claim 1 in the form of an emulsion of an organic liquid in the water.
3. A composition as claimed in claim 1 in the form of a dispersion solid resinous material in the water.
4. A composition as claimed in any one of claims 1-3 in which the resinous material is a thermally curable resinous material.
5. A composition as claimed in any one of claims 1-3 in which the resinous material is a photo-sensitive material.
6. A composition as claimed in claim 1 substantially as herein before described.

7. A method of making a patterned resist upon a substrate in the manufacture of a printed circuit board in which there is employed a coating composition as claimed in any one of the preceeding claims.
8. A method as claimed in claim 7 in which the resist is a solder resist.
9. A method as claimed in claim 7 substantially as herein before described.

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Examiner's report to the Comptroller under  
Section 17 (The Search Report)

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Relevant Technical fields

- (i) UK CI (Edition K ) C3B (BC, BF, BN); C3V (VAD, VAR, VAT, VABD, VABM, VABX)  
(ii) Int CI (Edition 5 ) C08G, C08L, C09D, G03F

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES:- DERWENT WPI, WPIL

Date of Search

26 FEBRUARY 1992

Documents considered relevant following a search in respect of claims

1-9

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2083044 A (NIPPON PAINT) See the whole specification	1-4
X	GB 1357029 (OWENS-CORNING) See page 5 line 18 to page 6 line 4	1, 3

SF2(p)

HD - c:\wp51\doc99\fil000112

Category	Identity of document and relevant passages	Relevant to claim(s)

#### Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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